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A resin composite material containing an eugenol derivative for intracanal post cementation and core build-up restoration

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Abstract

Objectives. To formulate and evaluate new dual cured resin composite based on the inclusion of eugenyl methacrylate monomer (EgMA) with Bis-GMA/TEGDMA resin systems for intracanal post cementation and core build-up restoration of endodontically treated teeth.

Methods. EgMA was synthesised and incorporated at 5% (BTEg5) or 10% (BTEg10) into dual-cure formulations. Curing properties, viscosity, T_g, radiopacity, static and dynamic mechanical properties of the composites were determined and compared with Clearfil™DC Core-Plus, a commercial dual-cure, two-component composite. Statistical analysis of the data was performed with ANOVA and the Tukey's post-hoc test.

Results. The experimental composites were successfully prepared, which exhibited excellent curing depths of 4.9, 4.7 and 4.2 mm for BTEg0, BTEg5 and BTEg10 respectively, which were significantly higher than Clearfil™DC. However, the inclusion of EgMA initially led to a lower degree of cure, which increased when measured at 24h with values

comparable to formulations without EgMA, indicating post-curing. The inclusion of EgMA also lowered the polymerisation exotherm thereby reducing the potential of thermal damage to host tissue. Both thermal and viscoelastic analyses confirmed the ability of the monomer to reduce the stiffness of the composites by forming a branched network. The compressive strength of BTEg5 was significantly higher than the control whilst flexural strength increased significantly from 95.9 to 114.8 MPa (BTEg5) and 121.9 MPa (BTEg10). Radiopacity of the composites was equivalent to ~3mm Al allowing efficient diagnosis.

Significance. The incorporation of EgMA within polymerisable formulations provides a novel approach to prepare reinforced resin composite material for intracanal post cementation and core build-up and the potential to impart antibacterial properties of eugenol to endodontic restorations.

1. Introduction

The restoration of endodontically treated teeth (ETT) remains a challenge in clinical practice, especially under conditions of extensive root canal flaring [1,2]. Factors such as caries, trauma to immature permanent teeth, anomalies, internal resorption, and over preparation may result in flared root canals with thin dentinal walls and open apices which make root canal debridement difficult and complicate the endodontic and restorative procedures [3,4]. In such cases, prefabricated fibre posts are often used to provide retention for the final coronal restoration. For luting procedures, the use of resin composite core materials with high modulus of elasticity is highly recommended because it can increase the fracture resistance of these weakened teeth and is an alternative to resin cements for one-stage post placement and core build-up restoration [5,6]. The modulus of elasticity of current luting cements are far lower than that of posts and dentine, which may create a zone of high stresses especially when a thick layer of cement is present in a wide or flared canal, leading to inefficient bonding [5,7].

More recently, dual cured resin composite materials with different viscosities have been used in combination with fibre posts to restore structurally compromised ETT [8]. Most of these materials are methacrylate resin based with high filler content and superior mechanical properties than those of resin cements. Previous studies have shown that incorporation of high amounts of filler improve the rigidity of the luting agent but increase stress development during polymerisation, which in turn affects the integrity of adhesive interface, reducing bond strength and increasing microleakage [9,10]. The higher viscosity that is associated with higher filler load [11] also impedes the injection of the material into the root canal producing gaps and voids that may provide a site for recurrent caries to develop. The composition of the matrix [12] also has an effect on both viscoelastic and rheological properties, which influence the contraction stress and microleakage of the direct restoration [13,14]. Consequently, the incorporation of low molecular weight monomers within methacrylate resin composite materials can enhance the flexural properties and lower viscosity [15].

On the other hand, numerous efforts have been made recently on the development of new monomers to be added into the formulation of dental resin composites with the aim of improving their functionality, quality and durability. Several low viscosity ionic mono and dimethacrylate monomers containing quaternary ammonium groups such as 1,2-Methacryloyloxydodecylpyridinium bromide (MDPB) and bis(2-methacryloyloxyethyl) dimethylammonium bromide (IDMA) imparting antimicrobial properties in conjunction with existing dental dimethacrylate-based monomers have been reported [16,17]. However, adverse effects on mechanical properties associated with high monomethacrylate content were found. In addition, some of the quaternary ammonium based monomers exhibit miscibility problems with hydrophobic dimethacrylates [17].

Eugenyl methacrylate monomer (EgMA), a low molecular weight monomer obtained by modifying the chemical structure of eugenol was reported by Rojo et al [18], which has a polymerisable methacrylate group that allows facile free radical polymerisation reaction while impair desired functionalities [18]. Furthermore, previous studies on rheological

properties of the EgMA copolymers confirmed the formation of branching structures with a range of degree of crosslinking that were responsible for the elastic or viscoelastic properties of these systems. In addition, this monomer also demonstrated intrinsically bactericidal properties against different microorganisms including *Streptococcus mutans* [19], which is involved in composite failures associated with secondary caries [20,21].

The purpose of this study was to formulate and characterise new dual cure resin composite materials based on EgMA monomer and Bis-GMA/TEGDMA resin systems for endodontic post cementation and core build-up restoration. The addition of this monomer was expected to enhance the viscoelastic properties, the mechanical response of the composites and potentially impart some antibacterial property to the resin system by virtue of the EgMA residues [19]. The influence of this monomer on curing kinetics, viscosity, physical and mechanical properties of the experimental composites are reported and the results compared with those of a commercially available dual cured resin composite core material.

2. Materials and Methods

2.1. Materials

2, 2-Bis [4- (2-hydroxy-3 methacryloyloxypropyl)-phenyl] propane (Bis-GMA) and tri-ethylene glycol dimethacrylate (TEGDMA) were purchased from Esschem Europe Ltd (Durham, UK). Benzoyl peroxide (BPO) and A-174 silane coupling agent (3-Trimethoxysilyl propylmethacrylate) were supplied by Merck (Frankfurt, Germany). Methacryloyl chloride (95%) was purchased from Alfa Aesar, UK. Camphoroquinone (CQ), N, N - dimethyl-p-toluidine (DMpT), eugenol and trimethylamine were purchased from Sigma-Aldrich, Company Ltd, Dorset, UK. The fillers used in this study were hydroxyapatite (HA, Plasma Biotol Ltd., Tideswell, Derbyshire, UK) and zirconium oxide (ZrO₂, Fisher Scientific Ltd., Loughborough, UK) with a mean particle size diameter of 3-5 µm and 18 µm respectively, which were silanized according to the method described elsewhere [22]. Solvents used were

of HPLC grade from Acros-Organics UK. All other reagents were purchased from Sigma Aldrich and used as received, except BPO that was purified by fractional crystallisation from ethanol. A commercially available resin composite material (Clearfil™DC Core plus, Kuraray, Tokyo, Japan) was used as a commercial reference.

2.2. Synthesis and characterization of Eugenyl Methacrylate

EgMA monomer (MW = 232.23 g/mol) was synthesised as reported previously by Rojo et al [18]. In brief, eugenol (0.061 mol) and triethylamine (0.061mol) were dissolved in 50 ml of dichloromethane. Methacryloyl chloride (0.076 mol) was dissolved in 10 mL of dichloromethane and then added drop wise whilst the reaction mixture was kept in an ice bath under magnetic stirring for 48 hours. The triethylamine chlorhydrate formed was then removed by filtration and the mixture washed with NaOH (5% w/v), neutralised with saturated NaCl and subsequently dried over anhydrous MgSO₄. The solvent was then filtered and removed under reduced pressure and the product purified by flash chromatography using a mixture of ethyl acetate / hexane (10/90 v/v) as an eluent. The EgMA monomer was characterised by ATR-FTIR (ATR-Perkin-Elmer-Spectrum One) and ¹H-NMR (Bruker-300 MHz) spectroscopies. The FTIR spectrum was recorded in the 4000 cm⁻¹ to 650 cm⁻¹ region with a wavenumber step of 0.5 cm⁻¹. ¹H NMR spectra were recorded at 25 °C and deuterated chloroform was used as a solvent.

2.3. Preparation of composites

Three different experimental composites namely BTEg0, BTEg5 and BTEg10 were prepared and their respective composition is listed in Table 1. Briefly, a batch of monomer mixture was first prepared and divided in two separate pastes and the initiator and activator were added respectively to avoid self-polymerisation. Then the corresponding amount of silanized fillers was added to each paste and mixed by magnetically stirring for 24h. After complete wetting of the fillers, the pastes were sheared with a Teflon spatula against a glass

slab surface in a dark room to ensure thorough dispersion of fillers in the resin. Subsequently, equal masses of the two pastes were hand-mixed using a stainless steel spatula for 30 seconds and carefully placed into different moulds avoiding bubble entrapment. The upper and lower surface of the mould was covered with glass slides and then cured by visible light for 40 s each side by overlapping, using Optilux 501 (Demetron, Danbury, USA) dental curing unit with an irradiance of $400 \pm 50 \text{ mW cm}^{-2}$. The Clearfil™DC commercial reference was mixed according to the manufacturer's instructions, moulded and cured by the same procedure described above.

2.4. Viscosity of the uncured composites

The viscosity of the experimental composite pastes were determined at 25 °C at different shear rates using a digital viscometer (Brookfield DV-E; Middleboro, USA) with a SC4-14/6R spindle configuration and $\pm 0.1\%$ accuracy. The viscosity value for each paste (2.1 ml) is reported in milliPascal/second (mPa·s) for a 2 minutes time span; with the measurement repeated twice for each composite.

2.5. Degree of conversion

In order to assess the degree of cure of the composites, FTIR spectra of the resins were recorded before and after cure using a FTIR spectrometer with an ATR attachment (Perkin-Elmer, USA). Spectra were obtained over $4000\text{--}650 \text{ cm}^{-1}$ region and acquired with a resolution of 4 cm^{-1} and a total of 16 scans per spectrum. The spectra of the polymer were obtained by curing a small amount of each composite between two translucent Mylar strips, which were pressed to produce a very thin film. Three cured specimens of each group were tested 10 minutes after curing and after 24h storage at 37 °C. The degree of cure was then determined using the equation 1

$$\text{Degree of conversion (\%)} = \left[1 - \frac{\left(\frac{A_{1637}}{A_{1608}} \right)_{\text{polymer}}}{\left(\frac{A_{1637}}{A_{1608}} \right)_{\text{monomer}}} \right] \times 100 \quad (\text{Eq1})$$

where A_{1637} and A_{1608} correspond to the absorbance of the aliphatic $\nu_{C=C}$ and aromatic $\nu_{C=C}$ peaks registered at 1637 cm^{-1} and 1608 cm^{-1} respectively before and after polymerisation.

2.6. Curing parameters

The depth of cure and maximum curing temperature of the resin composites were determined in accordance with the respective standard ISO4049 [23] and ISO5833 [24] techniques. Briefly, composite materials ($n=3$) were filled in a white Teflon mould with a cylindrical cavity of 15 mm height and 4 mm diameter while the top of the mould was covered with a transparent polymer strip. The specimens were then polymerised for 40 s from the top side. Immediately after irradiation and removal from the mould, the unpolymerised parts were scraped off with a plastic spatula. Subsequently, the depth of the cured material was measured with a digital calliper (DURATOOL, UK) in three places and an average was obtained. The absolute length was divided by two; the average of three measurements was then reported as the depth of cure.

A thermocouple (1.3 mm diameter) fitted to a high-sensitivity temperature recorder (KM1242, Herts, UK) was used to measure the polymerisation exotherm. The wire was placed centrally in a cylindrical Teflon mould filled with each material and its stripped ends were levelled with the surface to be irradiated. The materials were polymerised for 40 s with an irradiance of $400 \pm 50\text{ mW cm}^{-2}$ from one side and the maximum temperature was reported during the polymerisation cycle. Three measurements were done for each material at room temperature.

2.7. Thermal properties

Glass transition temperature (T_g) of the experimental composites was measured on a Differential Scanning Calorimetry (DSC, Perkin Elmer) and determined as the midpoint of the heat capacity transition registered. Samples of approximately 10 mg were introduced in the

aluminium pans and heated from 0 °C to 230 °C at the rate of 20 °C/min in an inert N₂ atmosphere and two repeats were performed for each composite.

2.8. Dynamic mechanical analysis (DMA)

Storage (E') and loss modulus (E'') as function of temperature were determined for the cured composites using Dynamic Mechanical Analysis (DMA) (Perkin-Elmer, DM8000). A frequency of 1 Hz was applied and a temperature range between 25 °C and 185 °C (heating rate of 2 °C/min) was selected. Rectangular specimens were fabricated for DMA test by filling a Teflon mould (2 × 2 × 40 mm) with unpolymerised material, which was then light cured with an irradiance of 400 ± 50 mW cm⁻² following the same procedure mentioned earlier. Three samples for each group were tested and mean values are reported.

2.9. Mechanical properties

2.9.1. Flexural properties

Three-point bending test was carried out according to the ISO 4049 [23] using a universal testing machine (Instron model 5569A-Series Dual Column, High Wycombe, UK) at a cross-head speed of 1 mm/min with span length fixed at 20 mm. Six specimens with dimensions (2 × 2 × 25 mm) were fabricated using a Teflon mould and tested after 24 h of storage at 37 °C. Flexural strength (σ) and flexural modulus (E) were calculated using equations 2 & 3 respectively.

$$\sigma = \frac{3FL}{2bh^2} \quad (\text{Eq2})$$

$$E = \frac{L^3}{4bh^3} \times \frac{F}{Y} \quad (\text{Eq3})$$

where F = maximum strength, L = distance between the rests, b = width of the specimen, h = height of the specimen, and F/Y = slope of the linear part of the stress– strain curve.

2.9.2. Compressive strength

Six cylindrical specimens (6 x 4 mm) were prepared and tested after 24 h maintained dry at 37 °C using a universal testing machine at a cross-head speed of 1 mm/min. Compressive strength (S) was calculated using equation 4

$$S = \frac{F}{(d/2)^2 \times \pi} \quad (\text{Eq4})$$

where, F = maximum strength and d = diameter of the specimen.

2.9.3. Microhardness test

Knoop microhardness measurements were carried out on the composite samples ($n = 6$) with a Durimet microhardness tester (Leitz, Wetzlar, Germany) using a load of 100 g for 15 s. Three measurements were made per sample and the mean values are reported.

2.10. Fracture surface examination

The fractured surfaces of the three point bend test specimens were analysed using Scanning Electron Microscopy (SEM, Hitachi High Technologies, S-3500N) at an accelerating voltage of 10 KeV and magnifications 2000x and 5000x. The fracture surface of tested samples was coated with gold using sputter coater before analysis.

2.11. Radiopacity

Five discs (15 mm diameter × 1 mm thick) were prepared from each composite group, and digitally photographed alongside a high purity aluminium step-wedge (1100 alloy) with thickness varying from 1 to 10 mm with increments of 1 mm as a reference according to ISO 4049 [23]. The images were taken using dental X-ray unit (Heliodent; Sirona, Bensheim, Germany) operating at 70 kV, 8 mA, and 0.2 seconds) with phosphor plate system (Digora® Optime; Soredex, Tuusula, Finland) to get a radiograph. The radiopacity of the experimental material was determined by comparison with the opacity of aluminum step-wedge. A free

image editing software (ImageJ processing and analysis in java, version 1.47v) was used to measure the grey value of the sample and aluminium in the resulting images.

2.12. Statistical analysis

A one-way (ANOVA) and Tukey's post hoc test were employed for the statistical evaluation of the data at a level of significance $p < 0.05$. Values that were significantly different with respect to the control formulation (BTEg0) and the commercial (Clearfil™DC Core) material are marked with one asterisk (*) or two asterisks (**) respectively in the corresponding results.

3. Results

3.1. Synthesis and characterization of Eugenyl Methacrylate

Eugenol methacrylate was synthesised by reacting eugenol with methacryloyl chloride, using triethylamine as a catalyst with a yield of 80%. The FTIR spectra of EgMA is shown in Figure 1 and the absorption bands arising at 1725 cm^{-1} (C=O carbonyl stretching vibration) and 1637 cm^{-1} (C=C in the acrylic and allyl groups) confirm the conversion of eugenol to eugenyl methacrylate. The stretching frequency at 1608 cm^{-1} (C=C aromatic) is due to the unsaturated aromatic ring, the peak at 1434 cm^{-1} can be attributed to $\text{CH}_2=$ in the allyl group and the strong peak at 1120 cm^{-1} assigned to C–O stretching from ethers. The molecular formula and $^1\text{H-NMR}$ spectrum of the monomer are shown in Figure 2. The peak assignments δ (ppm) are as follows: δ_{H} 7.0 ($\text{H}_5\text{-Ar}$), 6.8 ($\text{H}_{3,6}\text{-Ar}$), 6.4 and 5.7 ($\text{CH}_2^\beta=\text{C}$), 6.0 - 5.8 ($\text{CH}=\text{CH}_2$), 5.1 ($\text{CH}=\text{CH}_2$), 3.8 ($\text{CH}_3\text{-OPh}$), 3.4 (CH_2Ph), 2.1 (CH_3^α).

3.2. Viscosity

The experimental composite materials exhibited a decreasing viscosity with an increasing shear rate as shown in Figure 3. This pseudoplastic or shear thinning behaviour was more pronounced with increasing content of EgMA monomer in the formulations.

3.3. Curing parameters

The degree of conversion, curing depth and polymerisation exotherm of all materials tested in this study are shown in Table 2.

The degree of conversion for each formulation was calculated using equation 1 and the values ranged between 64 to 72% (Table 2). Incorporation of EgMA monomer at 10% into composites formulation decreased the degree of conversion initially, however, there were no significant difference in DC between composites containing EgMA and the control at 24h post curing. The experimental composites exhibited comparable depths of cure among them but their values were significantly higher in comparison to the commercial composite ($P < 0.05$). The inclusion of EgMA in the formulation also lowered the polymerisation exotherm with increasing concentration at 10% (Table 2).

3.4. Thermal analysis

The DSC thermograms for the experimental composites are shown in Figure 4. Composites containing EgMA monomer exhibited T_g values ranging between 106 ± 4.2 °C and 114 ± 3.5 °C which were slightly lower than that of the composite without EgMA (119 ± 2.1 °C). However, no significant differences in T_g were found between experimental composites ($P > 0.05$).

3.5. Dynamic mechanical analysis (DMA)

Figure 5 illustrates the evolution of $\tan \delta$ with the temperature for experimental composites and the commercial material. The mean values of storage modulus (E'), loss modulus (E'') and damping factor ($\tan \delta$) at 37 °C were extracted from DMA curves and presented in Table 3. There were no statistically significant differences ($P > 0.05$) in the E'' and $\tan \delta$ due to the presence of EgMA in the experimental composites while the storage modulus of 10% EgMA formulation were significantly lower than the control. At 37 °C the commercial

composite showed statistically significant lower Tan δ value than the experimental composites while at higher temperatures Clearfil™DC Core exhibited a higher Tan δ peak.

3.6. Mechanical properties

The results in Table 4 show that the addition of EgMA into the composite formulations increased both flexural and compressive strength. The statistical analysis showed no significant difference in the flexural modulus of the experimental materials ($p>0.05$), whilst the flexural strength of both EgMA formulations and the compressive strength of 5% EgMA formulation were significantly higher than the control. The microhardness of BTEg10 (10 wt.% EgMA) composites was significantly lower than that of control ($p<0.05$). The mechanical properties of the experimental formulations were comparable to that of the commercial composite except for the microhardness which was significantly lower ($p<0.001$).

3.7. SEM of the fracture surface of the composites

Representative SEM images of the fractured surfaces of the flexural test specimens from each of the three experimental groups are shown in Figure 6. Variance was detected between the control and the remaining experimental groups. The incorporation of EgMA monomer resulted in less fillers agglomeration and the particles were well dispersed into the resin matrix.

3.8. Radiopacity

Figure 7 shows the radiopacity of the experimental and commercial composites with the grey-scale value of aluminium step wedge measurements in (mm AL). All the composites exhibited a favourable radiodensity values around 3 mm Al that satisfy the ISO 4049 specifications and were significantly higher than that of commercial composites ($p<0.05$). The radiopacity of BTEg10 composites was significantly higher than that of control (BTEg0) at $p<0.05$.

4. Discussion

New dental resin composite with methacrylate derivative of eugenol was developed for intracanal post cementation and core build-up. The incorporation of this derivative provided an improvement in the initial handling viscosity, polymerisation exotherm, mechanical strength, viscoelasticity and radiopacity, while slightly reduced the initial degree of cure and Tg. A significant reduction in storage modulus and microhardness was also observed at higher concentration.

Eugenol methacrylate monomer was synthesised by a typical acylation reaction as described earlier by Rojo et al [18]. The modification of the chemical structure of eugenol through the phenolic group allows it to participate in polymerisation reactions rather than to inhibit them. The EgMA monomer showed typical peaks arising due to the carbonyl and the allyl group in the FTIR spectrum that confirmed the methacrylation of eugenol. The ^1H NMR spectra showed the resonance signal corresponding to the proposed structure illustrated in Figure 2 and the absence of the characteristic phenol peaks at $\delta_{^1\text{H-NMR}}$ 5.5 ppm confirmed the reaction of eugenol.

The miscibility of comonomers within a polymerisable mix is important to overcome phase separation post polymerisation. The monomer EgMA exhibited complete miscibility with Bis-GMA/TEGDMA mixtures and there was no evidence of phase separation. The composition of the experimental composites were based on a set of design of experiments with monomers Bis-GMA used for imparting stiffness and lower shrinkage, TEGDMA to lower viscosity and allow crosslinking and EgMA as a polymerisable monomer derivative of eugenol. The selection of EgMA contents within the experimental formulations was based on previous studies which demonstrated that 10 wt.% of EgMA is enough to impart the mechanical and biological benefits of the eugenol residues with absence of cyto or genotoxic effects. The cytotoxicity of the monomer has been reported earlier and was comparable to those observed for other monomers commonly used to prepare analogue restorative dental

materials [18]. Furthermore, the cytocompatibility of EgMA containing polymer matrices have also been reported previously [46] showing the absence of residual monomers and very good cytocompatibility.

The low viscosity of the EgMA monomer also functioned as an excellent diluent for Bis-GMA and enhanced the initial handling viscosity allowing easy dispersion of the fillers within the resin matrix. This is a common finding for most organic fluids, which may be attributed to temporary deformation and alignment of the flexible molecules in the streamlines of increasing flow. A low viscosity of these composites during the working period is also desirable as it can facilitate their injection into the root canal through the delivery devices, and for effective impregnation of dentinal substrates and post surface [25]. It also reduces the polymerisation shrinkage stress within the material during early setting [26,27] and the stress relief via resin flow relaxation can reduce the possibility of gap formation [14] and marginal leakage [28, 29], which can enhance the longevity of the restorations. It has also been reported that the lower viscosity resin composites provide significantly higher adhesion to post surface attributed to higher intrusion on the substrates [8].

The composite formulations with 65% by weight of fillers were used for all formulating composites based on flowability. The selection of the fillers used in the composite formulation stemmed from the excellent established biocompatibility of these fillers, the ability to enhance the modulus of polymers, in addition hydroxyapatite being similar to the mineral component of dentine and ZrO_2 functioning as a radiopacifying agent [30,31]. The weight fractions of the fillers were selected on the basis of optimal properties and radiographic appearance. Moreover, the homogenous distribution and the stable dispersion of the fillers without any sedimentation, demonstrated the stability of the composite mixtures at the different storage periods. The experimental composite was designed as dual-cured resin system with better clinical handling as it allows extended working time and secures polymerisation in deep parts of the canal [32-34].

The degree of cure were found to be above the minimum acceptable values for clinical use (>55%) [35] that were comparable with other dual-cured dimethacrylate based composites [36]. The significant reduction in the degree of conversion observed 10 min post curing (Table 2) of composites containing 10% EgMA with respect to control is the consequence of the bi-functional nature of acrylic and allylic double bonds in the EgMA moiety, which further confirms the participation of the monomer during the bulk polymerisation [37] leading to either branching or crosslinked structures with unreacted allylic bonds from the pendant eugenyl moiety. However, the degree of cure increased when measured at 24h with values comparable to formulations without EgMA indicating post-curing. Nevertheless, it is important to highlight that the post curing polymerisation observed was very limited indicating that most of post-irradiation polymerization occurred in the first few minutes after light exposure [38,39].

The curing depth values of the experimental composites exhibited statistically significant higher values in comparison to the commercial composite. This difference was associated with composition, catalyst type and concentration and also transmission coefficient which depend on the shade of the resin [40]. Curing depth, depends on the type and concentration of initiator used, irradiation conditions and material composition (including opacity) [41,42]. Here, the use of the same irradiation conditions and the same concentration of photoinitiator (0.5% by wt. of resin mixture) in the formulation of dual-cure composites resulted in statistically similar curing depths of the experimental composites. However, the progressive reduction with the content of EgMA was attributed to the increase of opacity of these composites that reduce the light transmittance [43].

The addition of EgMA decreased the maximum curing temperature; being more pronounced for BTEg10 formulation, which exhibited a peak temperature of 31.4 °C and was significantly lower than the control and commercial material. This reduction in the exothermic polymerisation of the composite material without compromising the mechanical properties

constitutes an additional advantage preventing thermal damage on adjacent root dentine whilst the curing occurs within the endodontic cavity.

The glass transition temperature of the composites containing EgMA exhibited lower T_g , which can be attributed to the lower T_g of EgMA homopolymer (about 95 °C) [18] in comparison with the other methacrylate derivatives in the composite (Bis-GMA and TEGDMA). However, all the experimental composites post curing showed T_g values much higher than the oral cavity would normally be exposed to, thus ensuring no softening or hardening during clinical function.

DMA was used to measure the viscoelastic properties at a frequency and temperature range experienced in the oral cavity. The experimental composites containing 10% EgMA (BTEg10) exhibited a significantly lower E' due to the molecular flexibility by virtue of the higher EgMA component, however this effect was not observed in the composites containing 5% EgMA (BTEg5) due to the lower concentration. As the temperature was increased, the $\tan \delta$ remained constant for all experimental composites indicating higher damping and thermal stability. This is attributed to the silanation of the fillers that enhances the interfacial adhesion with the matrix in addition to the formation of a slightly cross-linked network in composites containing EgMA. Clearfil™DC Core, the commercial material was tested under identical conditions, showed the lowest value for $\tan \delta$ and the highest E' indicating the stiffness of these materials as consequence of the filler higher content (74 wt.%). Therefore, in accordance with previous studies, the viscoelastic properties of experimental composites offer a considerable advantage over the commercial composite material with respect to polymer network's ability to relieve the shrinkage stress through chain viscoelastic relaxation at normal oral temperature [44] and to their thermal stability at the more challenging environment of the oral cavity and therefore rendering better luting ability [45].

The static mechanical tests results showed that the EgMA monomer increased the resistance of composites against bending and compression stresses. This is consistent with

the results obtained from DMA which confirm the effect of EgMA, which allows for both crosslinking and forming branched structures. The crosslinked networks arising due to TEGDMA and EgMA from both EgMA lead to strengthening whilst an increase in ductility is observed due to the branching. However, it is evident that an optimum concentration of EgMA results in an increase of both compressive and flexural strength. It has been shown in previous studies that increasing monomer concentration beyond certain limits does not lead to further improvement in mechanical properties [37,46]. However, the mean values for flexural strength and compressive strength of eugenyl containing composites were similar to that of the commercial material ($P>0.05$). The KHN of Clearfil DC Core material was significantly higher than that of the experimental composites. The hardness of composite resins reflects their molecular chain flexibility and degree of polymerisation [47,48] and is affected by other factors such as resin matrix type, filler type and filler load [49,50]. Not only is the filler content in Clearfil DC Core is much higher, the type of filler is different than that of the experimental composites, which may account for lower microhardness. The Knoop hardness of BTEg10 was statistically lower than BTEg5 and BTEg0 ($p < 0.05$), however, the values obtained were in the range accepted for clinical applications [51].

Scanning electron micrographs of the fracture surfaces revealed homogenous distribution of the filler particles and good adhesion between the matrix and the filler in the experimental composites. In particular, EgMA containing composites appeared to show less debonding of the filler particles, which were also smeared by the matrix in comparison with the control (Figure 6). These findings suggest a better adhesion and diffusion of the monomer between the particles that provides a uniform distribution and homogenous matrix [52].

Radiopacity of luting resin composites and core materials is important for the clinician for accurate placement and follow up. According to ISO 4049 specifications, the radiopacity of dental composite material should be higher than, or at least equal to, that of the same aluminium thickness which is close to that of dentine. The radiopacity values of the experimental composites were significantly higher than that of commercial Clearfil™ DC Core

material and superior to those of enamel and dentine reported in previous studies which range between 1 and 2 mm Al respectively [53,54]. The higher radiocontrast of the experimental composites is likely due to the incorporation of zirconia and hydroxyapatite. The addition of EgMA monomer enhanced the filler dispersion within the resin matrix resulting in homogenous mixture which had a significant effect on radiopacity of BTEg 10 composite.

Further studies *in vitro* are needed to evaluate the performance of these composites in restoring structurally compromised ETT in term of bonding ability and reinforcement.

5. Conclusions

Resin composite containing eugenol methacrylate derivative EgMA, was obtained by dual polymerisation mechanism that exhibited outstanding properties in term of handling viscosity, flexural strength, viscoelasticity and radiopacity as potential new materials for post cementation and core build-up restoration in structurally compromised ETT with remarkable enhanced features in comparison with currently used dental composite materials. Therefore, they constitute a novel approach to include these resins with the biological benefits of eugenol that until now has been considered to be incompatible with in situ polymerising dental resin composites.

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Table 1 – Formulation codes and composition (% w/w) of experimental composites.

Composites	Monomers (wt %)			Fillers (by wt %)
Name	BisGMA	TEGDMA	EgMA	HA/ ZrO ₂ (4:3 wt:wt)
BTEg0	17.5	17.5	0	65
BTEg5	15.0	15.0	5	65
BTEg10	12.5	12.5	10	65

The initiators (0.5 % benzoyl peroxide + 0.5% camphorquinone) and activator (N,N dimethyl p-toluidine 1:1 molar ratio) were added as wt.% with respect to monomer of the final resin monomers blend (100 wt.%) formulation.

Table 2 –The degree of conversion (10 minutes and after 24 h post curing), depth of cure and polymerisation exotherm of the experimental composites and commercial material [mean (SD), n=3].

Composites	DC in % 10 min post cure (SD)	DC in % 24 h storage at 37 °C (SD)	Depth of cure in mm (SD)	Polymerization exotherm °C (SD)
BTEg0	72 (1.0)	73 (2.0)	4.9 (0.2)**	35.5 (0.2) **
BTEg5	68 (1.0) **	71 (1.0) **	4.7 (0.5)**	34.9 (0.3) **
BTEg10	64 (1.0) **, **	70 (2.0) **	4.2 (0.2)**	31.4 (0.4) **, **
Clearfil™DC	72 (2.0)	75 (1.0)	2.2 (0.1)	37.1 (0.3)

* Differences were statistically significant with respect to control BTEg 0 composite (p < 0.05).

** Differences were statistically significant with respect to commercial Clearfil DC Core material (p < 0.05).

Table 3 – Dynamic mechanical properties of the experimental composites and commercial material at 37 °C, 24h after curing [mean (SD), n = 3].

Composites	E' in GPa (SD)	E'' in GPa (SD)	$\text{Tan } \delta \times 10^3$ (SD)
BTEg0	120.2 (2.9)	7.9 (0.4)	66.5 (1.7)**
BTEg5	114.1 (2.5)	7.8 (0.3)	68.0 (1.2)**
BTEg10	104.7 (4.7)*,**	7.3 (0.2)	70.0 (1.4)**
Clearfil™DC	120.8 (2.1)	7.6 (0.2)	63.0 (0.6)

* Differences were statistically significant with respect to control BTEg 0 composite ($p < 0.05$).

** Differences were statistically significant with respect to commercial Clearfil DC Core material ($p < 0.05$).

Table 4 – Flexural modulus (FM), flexural strength (FS), compressive strength (CS) and Knoop hardness number (KHN) of the experimental composites and commercial material (mean (SD), n=6).

Composites	FM in GPa (SD)	FS in MPa (SD)	CS in MPa (SD)	KHN (SD)
BTEg0	11.4 (0.9)	95.9 (3.4)	198.2 (20.0)	39.3 (0.6) **
BTEg5	11.0 (0.8)	114.2 (9.4) *	234.6 (17.8) *	38.1 (0.9) **
BTEg10	9.8 (0.5) **	121.9 (11.0) *	214.6 (19.9)	34.0 (0.9) *,**
Clearfil™DC	11.5 (1.3)	110.5 (15.9)	210.9 (29.2)	54.6 (2.2)

* Differences were statistically significant with respect to control BTEg 0 composite ($p < 0.05$).

** Differences were statistically significant with respect to commercial Clearfil DC Core material ($p < 0.05$).

Figure 1

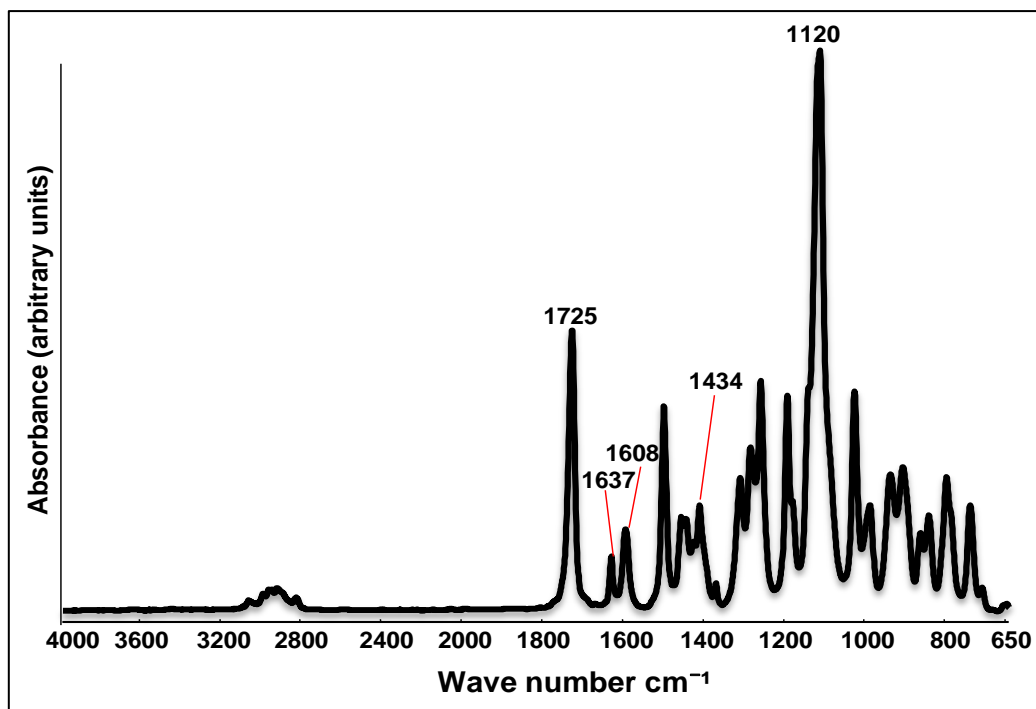


Figure1. ATR-FTIR spectrum of EgMA monomer. Vibrational peak assignments: $\nu_{\text{C=O}}$ 1725 cm^{-1} ; $\nu_{\text{C=C, Acryl}}$ & $\nu_{\text{C=C, Allyl}}$ 1637 cm^{-1} ; ν_{Ar} 1608 cm^{-1} ; $\nu_{\text{C-H, Allyl}}$ 1434 cm^{-1} and $\nu_{\text{C-O, Ether}}$ 1120 cm^{-1} .

Figure 2. Assignment and ^1H -NMR spectrum of EgMA monomer in CDCl_3 . Normalised integral values are displayed beneath the corresponding peaks.



Figure 3

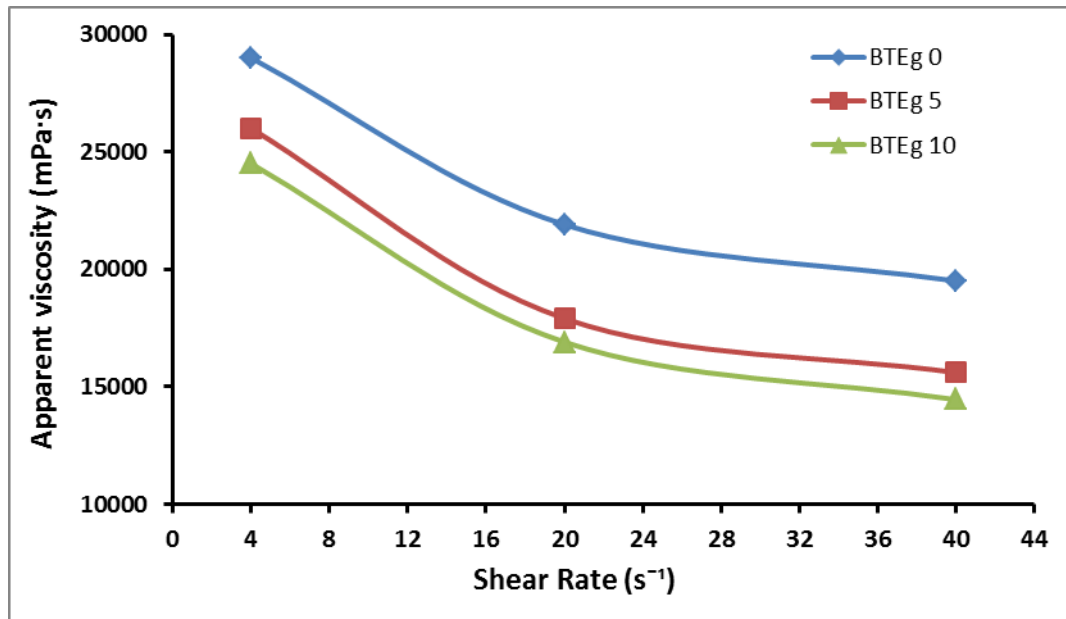


Figure 3. The apparent viscosity of uncured experimental composites at different shear rates.

Figure 4

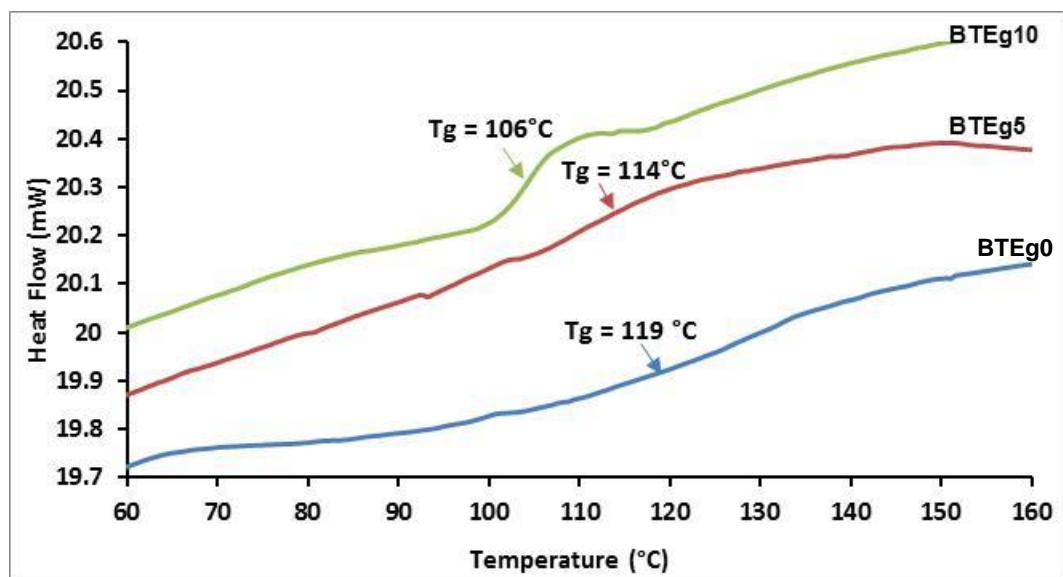


Figure 4. DSC representative curves of the experimental composites.

Figure 5

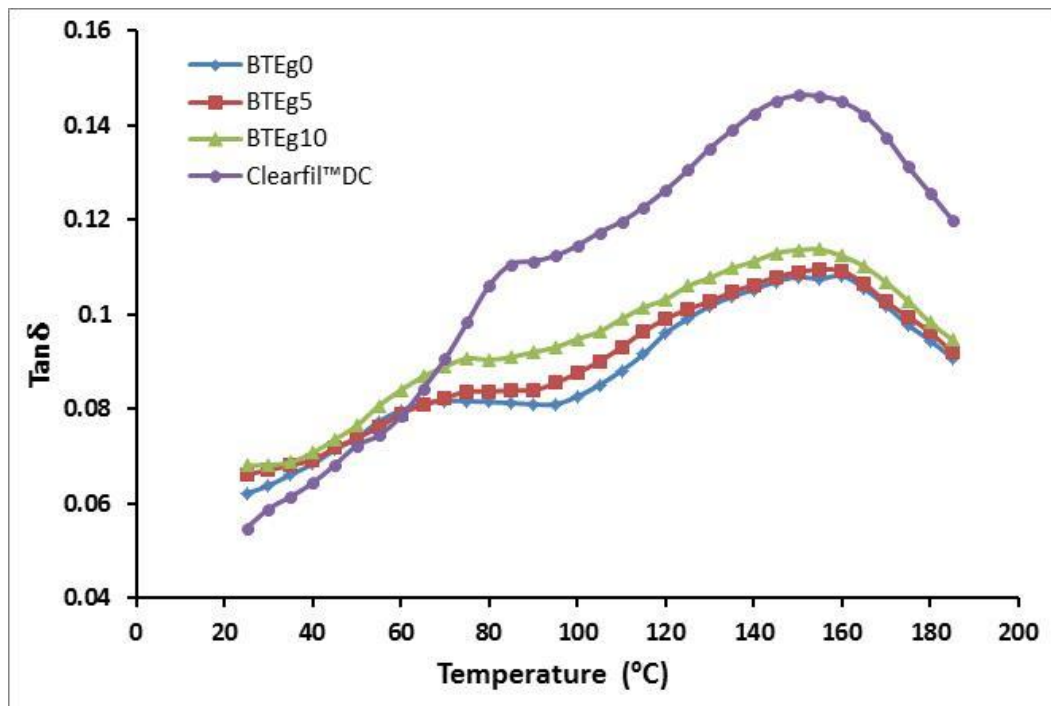


Figure 5. DMA curves for Tan δ of the experimental composites and commercial material.

Figure 6

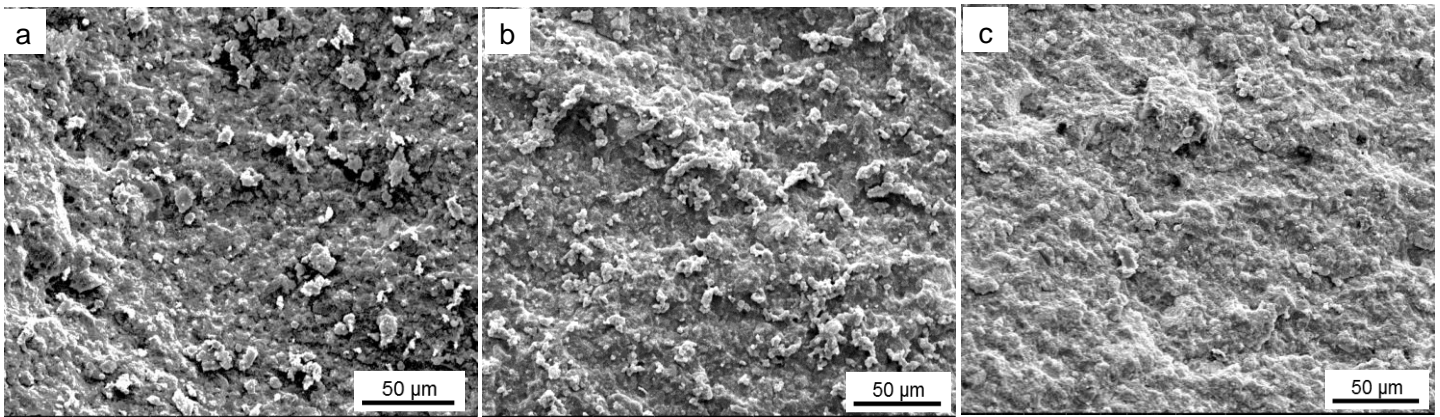


Figure 6. Representative SEM images of three point bending fracture surfaces of experimental composites (at 2000x magnification). (a) BTEg0 control, (b) BTEg5 and (c) BTEg10.

Figure 7

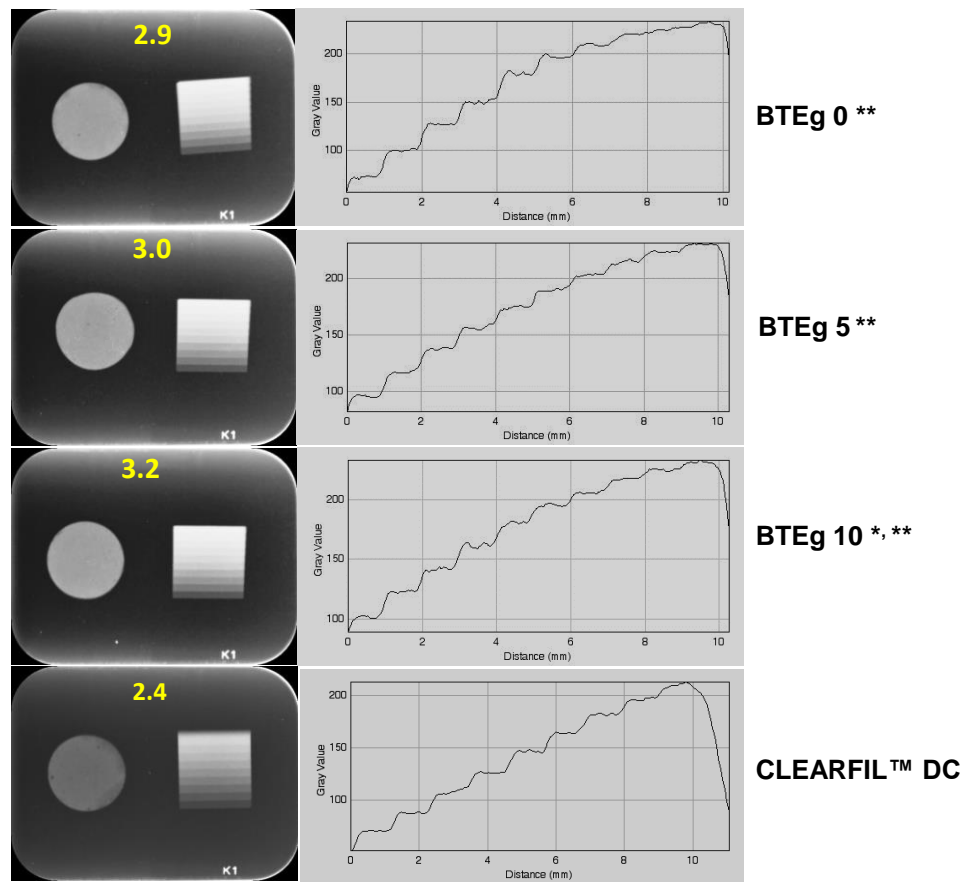


Figure 7. Representative radiographs of experimental composites and Clearfil™DC Core material in relation to the density of the aluminium step wedge (n=5).